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THE COMPOSITION OF THE SESQUICHLOROHYDRATE OF HYDROCYANIC ACID AND ITS SYNTHETIC APPLICATION

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Translation of "Ueber die Constitution des Sesquichlorhydrates der Blausaure und dessen synthetische Verwendung"
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THE COMPOSITION OF THE SESQUICHLOROHYDRATE OF HYDROCYANIC ACID AND ITS SYNTHETIC APPLICATION

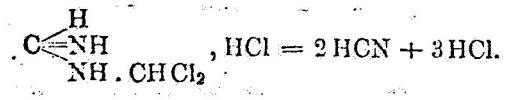
L. Gattermann and K. Schnitzspahn

ABSTRACT. Benzene was used in aldehyde synthesis with hydrocyanic acid. The reaction product was poured onto ice, forming a solid which, when boiled with alcoholic potash, produced benzhydrylamine. The sesquichlorohydrate was produced exactly according to Claisen's specifications. The progress of the reaction is described. Toluene results in a much more active reaction than benzene. Dimethylaniline was also employed, yielding the leuco-base.

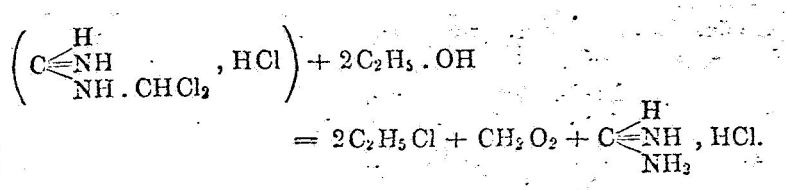
In the continuing process of synthesizing aldehydes with the help of hydro- /177
cyanic acid, our attention was directed to the sesquichlorohydrate of the hydrocyanic acid (2 HCN + 3 HCl) easily obtainable in quantitative yields by adding hydrochloric acid to a mixture of hydrocyanic acid and pure acetic ester, discovered by Claisen and Matthews [1]. Since this sesquichlorohydrate is a solid, odorless and almost non-toxic body, it seemed to us to be of practical interest to be able to use it instead of the toxic hydrocyanic acid. When we made our first tests in this direction, it had still not been definitely verified that aromatic hydrocarbons do not participate in the hydrocyanic acid synthesis. Therefore, we first worked with benzene, where a brisk reaction actually occurred with the development of hydrochloric acid. When we poured the reaction product on ice, we obtained a solid body which we at first took for the hydrochloride salt of benzaldyme. Only we were in nowise successful in separating benzaldehyde from it, so we soon came to the conclusion that we had an entirely different body in our hands. We do not wish to enumerate here the many wrong paths which we had to follow before we finally recognized its true nature, but prefer to communicate immediately the end result of our tests. When we boiled the reaction product with alcoholic potash, we found as an end product a very strong base, not volatile with steam which was determined as benzhydrylamine, $\frac{C_6H_5}{C_6H_5}>CH.NH_2$, will be shown below in more detail. As the two phenyl groups of this solid occurred instead of two chlorine atoms in the Friedel-Crafts' synthesis, it followed that a remainder of the compound $CHCl_2.NH_2$, i.e. Formamidchloride, must occur in the sesquichlorohydrate. If this fact is

*Numbers in the margin indicate pagination in the foreign text.

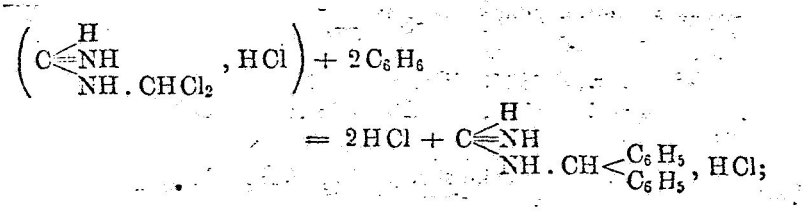
combined with disintegration of the body by alcohol, discovered by Claisen and Matthews, in which Formamidine occurs along with formic acid and chloric ether, it follows that the following constitution must be ascribed to the sesquichloro derivative of hydrocyanic acid:



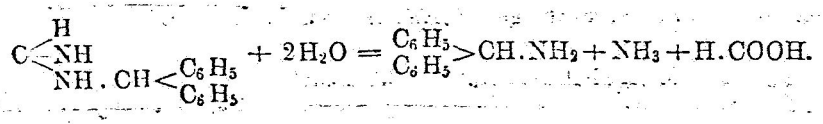
Accordingly this is to be understood as the hydrochloride salt of a dichloromethyl formamidine; this assumption actually explains all the reactions of the body. Thus, the decomposition with alcohol follows the equation below: /1771



When it is reacted with benzene in the presence of aluminum chloride, the following reaction is produced:



i.e. the benzhydryl formamidine is produced first, from which saponification finally leads to, along with ammonium and formic acid, benzhydrylamine:



Below the details of our tests will be briefly described.

The Sesquichlorohydrate of the Hydrocyanic Acid

The sesquichlorohydrate was produced exactly according to Claisen's specifications. For this purpose the mixture of hydrocyanic acid and acetic ester are in a vessel with walls as thick as possible, since the sesquichlorohydrate separates out in the form of such a solid scale that it can only be removed from the walls of the vessel by force. In addition, the substance is not as hydroscopic as it appears from Claisen's data. It is not at all necessary to melt it down in glass tubes, but it may be kept unaltered for months in glass closed with a tight glass stopper in a dessicator over sulphuric acid. The yield, almost quantiative, is from 200 g of potassium thiocyanide we get 35 g of pure hydrocyanic acid and 95 g of the chlorohydrate, while the theory demands

100 g.

Reaction on Benzene

Into a mixture of 11 g of benzene and 10 g hydrocyanic acid sesquichlorohydrate are gradually added 7 g of aluminum chloride, cooling being produced with ice water. Here a violent development of hydrochloric acid takes place and the reaction mixture is finally converted into a thick, viscous mass. The latter is then carefully poured into 150 ccm of ice water to which a few drops of hydrochloric acid have been added; the larger part of it is thus dissolved. If now concentrated hydrochloric acid is added to the solution, a colorless precipitate separates out which is filtered off, dissolved in water for purification and again precipitated with a corresponding amount of hydrochloric acid. More precise investigation showed that the hydrochloride salt of the benzaldehyde formamidine, $C\leqslant^{H}_{NH.CH<^{C_6H_5}_{C_6H_5}}, HCl$, was present in the bodies of which the structural equation was given above. /177

Computed C 68.15, H 6.08, N 11.36, Cl 14.40.
Found » 67.61, » 6.27, » 11.49, » 14.15.

The reaction progresses very smoothly, while 13 g of crude product, 87% of the theory, was obtained from the amount of sesquichlorohydrate used above.

If an aqueous solution of the salt is treated with platinum chloride, an almost insoluble double salt precipitates which crystallizes from dilute alcohol (1:1) in the shape of yellow needles with a melting point 210°.

$(C_{14}H_{15}N_2Cl)_2PtCl_4$. Computed Pt 23.68. Found Pt 23.51.

The free benzhydroformamidine precipitates from the aqueous solution of the hydrochloride salt onto an ammonium supplement in the form of white flakes which soon take on a crystalline structure and melt somewhat imprecisely at 118-120°.

$C_{14}H_{14}N_2$. Computed N 13.34. Found N 13.31.

If the amidine is boiled for a fairly long time with dilute soda lye, the NH-group will be replaced by O with the production of ammonium.

$$C\leqslant^{H}_{NH.CH<^{C_6H_5}_{C_6H_5}} + H_2O = NH_3 + C\leqslant^{H}_{O}\quad NH.CH<^{C_6H_5}_{C_6H_5},$$

and a body crystallizing into long, white needles with a melting point of 121-132° is obtained; this turned out to be identical with the formylbenzhydrylamine obtained by Leuckart and Bach (this journal 19, 2129) by heating benzophenone with formic acid ammonium.

If the amidine is heated with sodium hydroxide for a longer time, or if it is heated with alcoholic potash, a base is obtained which proved, by its boiling point and all other properties, to be benzhydrylamine. The latter greatly extracts carbon dioxide from the air and forms a carbonic acid salt which, as is known, melts at 91°. With phenyl mustard oil it is purified into phenyl benzhydryl thiocarbamine, which showed a melting point of 181°, as provided in the literature. The yield of benzhydrylamine amounts to about 80% of the theoretical, so that this new reaction may be quite proper as a method of preparing this body. /1773

Reaction on Toluene

The reaction of sesquichlorohydrate on toluene takes place much more actively than on benzene; therefore an excess of toluene is used as a diluting agent and the aluminum chloride is added with extreme care. If the reaction product is poured into a little ice water, a white, rather sticky mass separates; this is separated from the water, heated with water and an addition of a little hydrochloric acid until the toluene evaporates and the reaction product goes into solution. If concentrated hydrochloric acid or table salt is now added, the hydrochloride total hydroformamidine precipates for the most part in a melted state. If it is boiled for a longer time with aqueous or alcoholic potash, we get a base which boils at 317-318° (uncorrected), congeals on cooling, and crystallizes from ligroin in the form of stout needles with a melting point of 92°. This proved to be identical with the toluhydrylamine (for which the melting point of 93° has been given) obtained by Goldschmidt and Stocker (this journal 24, 2798) by reducing *p*-tolylketoxime. This proves that in the above Friedel-Craft's reaction the hydrogen atom in the para position has reacted with the methyl group of toluene.

$NH_2.CH(C_6H_4.CH_3)_2$.	Computed C 85.31, H 8.05, N 6.64. Found » 85.55, » 8.22, » 6.96.

If the crude amidine is now prepared directly on the base, the latter is obtained in a yield which not far from that theoretically demanded.

On being heated with acetyl acid anhydride it yields an acetylderivate which melts at 157-158°, while Goldschmidt and Stocker give its melting point as 159°.

With benzaldehyde we obtained a benzylide compound which is difficult to congeal. However, when we condensed the base with *p*-oxybenzaldehyde, we got a condensation product from alcohol with a melting of point of 187-188° crystallizing into pretty white needles.

$HO.C_6H_4.CH:N.CH.(C_6H_4.CH_3)_2$.	Computed N 4.44. Found » 4.51.

By heating this with phenyl mustard oil we obtained the phenyltolhydryl- /17
thiocarbamine which crystallizes from alcohol into needles with a melting point of 171°.

$C_{22}H_{22}N_2S$.	Computed S 9.25	Found S 9.15

Reaction on Dimethylaniline

We investigated this reaction in the hope of finally obtaining tetramethyldiamidebenzhydrylamine, i.e. the leuco-base of auramine. In the beginning the tests were carried out in the presence of aluminum chloride. However, it later proved beneficial to omit the aluminum chloride since, as in the formation of Michler's ketone from phosgene and dimethylaniline, condensation occurred here in the absence of aluminum chloride also.

Five g of sesquichlorohydrate were heated in an oil bath at 120-130° for three hours with 15 cm^2 of dimethylaniline; the reaction product was poured into water, rendered alkali with soda lye and the excess dimethylaniline blown off with steam. There remained behind in the flask a rather resinous black body from which the impurities were removed by heating with a little alcohol, at which time a solid crystallizing into white, silvery lustrous flakes remained undissolved. This crystallized from a mixture of benzene and ligroin in the shape of beautiful white needles which melted into a deep blue liquid at 173°. More precise research showed that the leuco-base of the auramine did not occur in it, but rather the crystal violet base, i.e. the hexamethyltriamide triphenylmethane, and that accordingly the primarily occurring benzhydrylamine derivate had reacted with a third molcule of dimethylaniline according to the following equation:

$$(CH_3)_2N.C_6H_4\underline{H + H_2N}.CH.[C_6H_4.N(CH_3)_2]_2$$
$$= NH_3 + CH[C_6H_4.N(CH_3)_2]_3.$$

$C_{25}H_{31}N_3$. Computed N 11.26 Found N 11.27.

The yield of leuco-base is good, since from the 5 g of sesquichlorohydrate used above, 9.1 g, i.e. about 80% of the theoretical, was obtained.

The syntheses [1] were predominantly carried out in our laboratories, and we have already obtained the aqueous reaction product, usually in white good yields, from *o*- and *m*-xylene, anisole, phenetole and other bodies.

Heidelberg, University Laboratory.

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[1] This has been registered for patent already by the die factories of the Friedr. Bayer & Co. in Elberfeld.